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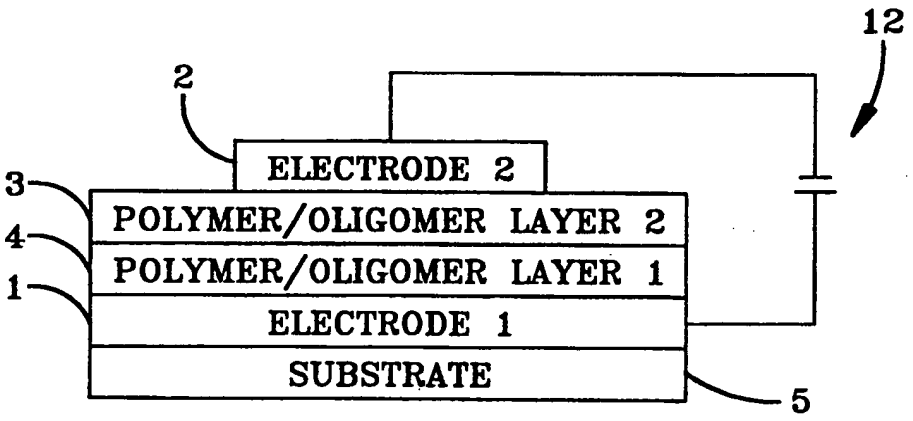
(54) Title: VOLTAGE CONTROLLED COLOR VARIABLE LIGHT-EMITTING DEVICES FEATURING MULTILAYERS OF DISCRETE POLYMER LAYERS AND MOLECULAR/OLIGOMER LAYERS



(57) Abstract

The present invention includes color variable light-emitting devices which are capable of generating two or more colors even at room temperature. The device is comprised of at least one active electroluminescent polymer layer (4) and one active electroluminescent molecular or oligomer layer (3).

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Voltage Controlled Color Variable Light-emitting Devices Featuring Multilayers of Discrete Polymer Layers And Molecular/Oligomer Layers

Technical Field:

This invention relates to multilayer light-emitting devices driven by electric field which are commonly referred to as electroluminescent devices.

Background:

In the past decade there has been great interest in electroluminescent devices. There have been several major embodiments of these devices including those built upon polymers known as polymer-based light-emitting devices (PLEDs), and devices made upon organic molecular or oligomeric units otherwise known as organic light-emitting devices (OLEDs). The nature of electroluminescence in such devices is determined by bandgap, interlayer interaction between polymer layers and interaction between molecules or between oligomers.

Among the limitations of present light-emitting devices is the difficulty in controlling color. In the usual configurations the devices only emit a single color. Recently there has been great interest in developing color variable light-emitting devices, i.e., devices that can generate two or more colors of light from a single pixel. In several device configurations have been demonstrated which produce multiple color light from a single pixel. These devices are either comprised of only polymers or of only organic molecules. Examples of the polymer-based devices are blends of polythiophene derivatives wherein different components of the blend emit different colors of light, the color of light varying with the applied voltage. A two color light-emitting electrochemical cell has been demonstrated as well. Color variable bipolar AC light-emitting devices have also been reported. Examples of red green and blue light emission from organic LEDs have been determined, for example by utilizing parahexephenyl as a blue light

generator which in turn stimulates either green or red emission from a second layer which coats part of the molecule layer.

It is desirable to be able to produce LEDs that allow for simple and inexpensive construction, and which provide for most efficient control of operation and color change.

Summary of the Invention:

The invention includes color variable light-emitting devices which are capable of generating more than one color even at room temperature. In general terms, the devices of the present invention comprise at least one layer of an electroluminescent polymer and at least one second layer comprising an oligomeric or molecular electroluminescent emitter; the two layers being sandwiched between a hole injecting electrode and an electron injecting electrode. In an optional embodiment of the present invention, additional hole transporting and/or electron transporting layers may be added to improve device operation and control of color. The color variability of the devices of the present invention may range in degree, varying from small spectral changes to obvious visible changes in color. The industrial applicability of the devices of the present invention is therefore broad, and will naturally vary with the degree of spectral change required or desired for each embodiment. For instance, devices of the present invention may be used for anything from visible displays to frequency modulation for signal transmission. Although, they may be used in a color variable mode (which characteristic is inherent), the devices of the present invention may also be used in a non-color-variable fashion by applying an essentially constant voltage.

The present invention also includes a method of producing a color-variable light from an electroluminescent device, the method comprising the steps: (1) obtaining a color variable

electroluminescent device of the present invention as described herein, and (2) causing sufficient current to flow into said device so as to cause the device to emit light, and varying the voltage of said current to a sufficient degree so as to cause a variation in the color of the light.

U.S. Patent Application Serial No. [to be supplied] by Epstein et al., entitled "Color Variable Bipolar/AC Light-Emitting Devices," and filed March 11, 1998, is hereby incorporated herein by reference, albeit that the devices of the present invention are used principally as unipolar devices.

General Structure

Figure 1 shows general schematic representations of optional variations in the structure of the devices in accordance with the present invention. Figure 1(a) shows a general schematic of a bilayer device which comprises two layers, with one layer being a polymeric layer as described herein, and another oligomeric or molecular layer as described herein (in Figure 1, the oligomeric or molecular layer is referred to simply as the oligomeric layer, but is to be understood as referring to either layer type). The layers may be in either orientation from top to bottom: polymeric/oligomeric(or molecular) or oligomeric(or molecular) /polymeric. Figure 1(b) shows a general schematic of a trilayer device which comprises three layers, with a first layer being a polymeric layer as described herein, a second layer being an oligomeric layer as described herein, and a third layer being of either material (in Figure 2, the oligomeric or molecular layers is referred to simply as the oligomeric layer, but is to be understood as referring to either layer type). Such layers may be in any order such as, from top to bottom, polymeric/oligomeric(or molecular)/polymeric or oligomeric(or molecular)/polymeric/polymeric, polymeric/polymeric/oligomeric(or molecular), oligomeric(or molecular)/oligomeric(or

molecular)/polymeric, etc. The constituent polymers, oligomers and molecules may be the same or different across respective layers.

The devices of the present invention may be fabricated by spin casting polymer layers on one electrode and then vacuum depositing the oligomer or molecular layer followed by vacuum deposition or sputtering of the second electrode. Although spin casting techniques are conventional and well known to the art, there are a wide variety of other well known methods that may be used to make a layered structure including Langmuir-Blodgett techniques, dip coating, doctor blading, etc.

The Polymers

The electroluminescent polymer(s) used in the polymeric layer(s) of the present invention, and the oligomer or molecular electroluminescent emitters used in the second layer of the present invention, may be any material adapted to perform the described function.

The polymeric layer may comprise a single polymer or a blend of polymers, the polymers selected from the group consisting of conjugated polymers, copolymers, and mixtures thereof. Examples of such polymers and their derivatives include those selected from several groups including, but are not limited to, conjugated and non-conjugated polymers and copolymers, including poly(pyridyl vinylene phenylene vinylene) (PPyVPV), polyvinylcarbazole (PVK), polypyridine (PPy), other polypyridines, polypyridylvinylenes, polythiophenes, polyphenylenes, polyphenylenevinylenes, rigid-rod polymers such as polyphenylenebenzobisthiozoles, poly-fluorenes, other polyvinylcarbazoles, polythienylenevinylenes, emissive polyacetylenes and blends and derivatives thereof, and so on. A wide variety of specific materials (i.e., derivatives) can be found in each of these groups as a result of modifications to the basic structure. As an

example, the emissive polymer layer may be a mixture of a polypyridylvinylene (i.e., having relatively greater electron transporting properties) and a polythiophene (i.e., having relatively greater hole transporting properties). Another example may be copolymers of emissive and non-emissive polymers such as polyethylenes.

The Oligomers and Molecules

The oligomer electroluminescent emitters used in the respectively described layers of the present invention may include any light-emitting, current conducting material adapted to perform the described function in the present invention and amenable to construction into devices of the present invention. As used herein, the terms "oligomer" or "oligomeric" are to be understood as referring to molecules having from 2 to no more than about 10 repeating units, preferably no more than ten repeating units. Such materials provide for ease of manufacture and also more uniform functional control of the LEDs they are used to form. Examples of such materials include parapentaphenyl, parasexiphenyl (6P), pentathiophene, sexithiophene, septathiophene, oligomers of stilbene and oligomers of bipyridine.

The molecular electroluminescent emitters used in the respectively described layers of the present invention may include any light-emitting, current conducting material adapted to perform the described function in the present invention and amenable to construction into devices of the present invention. Examples of such materials include quinacridone (QA), stilbene, rubrene, 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM), and 8-hydroxyquinone (Alq_3).

Figure 2 displays the repeat units of materials that may be used in the example embodiments of the present invention. These repeat units include those for parasexiphenyl (6P), poly(pyridyl vinylene phenylene vinylene) (PPyVPV), polyvinylcarbazole (PVK) and polypyridine (PPy).

The Electrodes

The electrodes used in the present invention may be selected from any electrode material appropriate for use in LED devices. Typically, these will include a hole-injecting and electron injecting electrode. It will be understood that reference to current flow will be understood as reference to the current facilitated by the layers of the devices of the present invention, which may be hole-injecting current or electron-injecting current, accordingly.

The hole injecting electrode typically may be fabricated from a number of relatively high work function conductors including indium tin oxide (ITO), gold and doped conjugated polymers such as doped polyaniline, doped polypyrrole and doped polythiophenes, and derivatives thereof. The electron injecting electrode typically is a relatively low work functioning metal such as aluminum, calcium or alloys thereof, such as magnesium-silver or lithium -aluminum. In some situations, higher work functioning metals such as gold may be used.

The hole injecting or electron injecting electrode may be placed upon a substrate which may be glass or may be insulating plastic, preferably clear. Examples of these devices are described below.

The Source of Electrical Energy

The devices of the present invention may be operated by any appropriate source of electrical energy 12 shown in Figure 1(a) and 1(b).

The light emitter of Figure 1(a) is also in electrical contact with a first electrode 1 and a second electrode 2 as described above, with the first and second electrodes arranged in spaced relation with each other. The first electrode 1 and the second electrode 2 are electrically connected to a potential difference supplied by source of electrical energy 12. That is, the first electrode 1 can be connected to a positive potential (anode) while the second electrode 2 is connected to a negative potential (cathode) or the connections can be reversed, with the first electrode connected to a negative potential while the second electrode is connected to a positive potential (opposite current direction). The device may reside on a substrate, such as substrate 5.

The polymer/oligomer layers 6 and 8 of Figure 1(b) are in electrical contact, respectively, with electrodes 9 and 10. Polymer/oligomer layer 7 is in electrical contact with polymer/oligomer layers 6 and 8. The first and second electrodes, 9 and 10, are electrically connected to a potential difference 12 as described above with respect to Figure 1(a).

The electrodes 1 and 2, and 9 and 10, are connected to a voltage source 12 by means of suitable electrical connectors or contacts. Such electrical connectors and contacts are conventional in the art and may include wire leads, printed circuit connectors, spring clips, snaps, solder, wrapped posts, conducting glues, etc. It is also to be understood that the electrical connector or contact can be the electrodes themselves. That is, the potential difference from current source 12 may be applied directly to the electrodes in which case electrodes may become the electrical contact or connector.

The devices of the present invention may feature a relatively low turn-on and operating DC voltage of less than about 36 volts. More preferably, a turn-on and operating voltage of less than about 18, less than about 9 volts, or even less than about 6 volts may been achieved. These

low voltages make these devices particularly advantageous for use in toys, as commercial light strips such as found on airplanes and in theaters, as signs, and as flat panel displays for computer and television use.

The voltage of the current from current source 12 may be varied sufficiently to vary the color of the light emitting from the device. The voltage of the current from current source may be varied using any appropriate voltage regulator device used in electrical arts. The amount of variation in voltage may be seen in the examples supplied herein.

The foregoing and other advantages of the invention will become apparent from the following disclosure in which one or more preferred embodiments of the invention are described in detail and illustrated in the accompanying drawings. It is contemplated that variations in procedures, processing, structural features, arrangement of parts, experimental design, ingredients, compositions, compounds, and elements may occur to a person skilled in the art without departing from the scope of or sacrificing any of the advantages of the invention.

Brief Description of the Drawings

Figure 1 shows schematically the structure of the a device in accordance with one embodiment of the present invention.

Figure 2 shows repeating units of materials that may be used in accordance with example embodiments of the present invention.

Figure 3 shows the EL spectra of a bilayer device ITO/6P/PPy/Al device in accordance with one embodiment of the present invention, operated under different applied voltages.

Figure 4 shows the current-voltage and luminance-voltage characteristics of a bilayer device ITO/6P/PPy/Al device in accordance with one embodiment of the present invention.

Figure 5(a) shows EL spectra of a three layer device, ITO/PVK/6P/PPy/Al, in accordance with one embodiment of the present invention.

Figure 5(b) is a CIE diagram of a three layer device, ITO/PVK/6P/PPy/Al, in accordance with one embodiment of the present invention.

Figure 6 shows the current-voltage and luminance-voltage characteristics of a three layer device, ITO/PVK/6P/PPy/Al, in accordance with one embodiment of the present invention.

Figure 7 shows the EL spectra of a bilayer device, ITO/PPyVPV/6P/Al, in accordance with one embodiment of the present invention, operated under different applied voltages.

Figure 8 shows the current-voltage characteristics of a bilayer device, ITO/PPyVPV/6P/Al, in accordance with one embodiment of the present invention.

Figure 9 shows EL spectra of a three layer device, ITO/PVK/PPyVPV/6P/Al, in accordance with one embodiment of the present invention.

Figure 10 shows the typical current-voltage (I-V) characteristics of a three layer device, ITO/PVK/PPyVPV/6P/Al, in accordance with one embodiment of the present invention.

Figure 11 shows the EL spectra of a three layer device, ITO/PPyVPV/6P/PPy/Al, in accordance with one embodiment of the present invention, operated under different applied voltages.

Figure 12 shows the current-voltage characteristics of a three layer device, ITO/PPyVPV/6P/PPy/Al, in accordance with one embodiment of the present invention.

Figure 13 shows the EL spectra of a bilayer device, ITO/6P/PPyVPV/Al, in accordance with one embodiment of the present invention, operated under different applied voltages.

Figure 14 shows the current-voltage characteristics of a bilayer device, ITO/6P/PPyVPV/Al, in accordance with one embodiment of the present invention.

Figure 15 shows EL spectra of a three layer device, ITO/PVK/6P/PPyVPV/Al, in accordance with one embodiment of the present invention.

Figure 16 shows the typical current-voltage (I-V) and luminance-voltage characteristics of a three layer device, ITO/PVK/6P/PPyVPV/Al, in accordance with one embodiment of the present invention.

Figure 17 shows the EL spectra of a bilayer device, ITO/PVK/6P/Al, in accordance with one embodiment of the present invention.

Figure 18 shows the current-voltage and luminance-voltage characteristics of a bilayer device, ITO/PVK/6P/Al, in accordance with one embodiment of the present invention.

Detailed Description of the Preferred Embodiments

In accordance with the foregoing summary of the present invention, the following describes in detail several embodiments of the present invention, which include what is presently considered to be the best mode.

In the examples shown below, the polymer layers were formed using spin coating techniques and the oligomer layer, typically parasexiphenyl (6P), was formed using vacuum deposition technique. The solvents used for the polymers are xylenes for PPyVPV; tetrahydrofuran (THF) for PVK; formic acid for PPy. The concentration is typically 5-10 mg/ml. In the device structure denoted as ITO/PVK/6P/PPyVPV/Al, for instance, the fabrication procedure is as follows. The PVK layer was first spin coated at ~ 3000 rpm from THF solution

onto a precleaned patterned ITO (with a sheet resistance of ~ 15 Ohm/square) at a pressure below 10^{-6} torr. The 6P layer was then thermally evaporated onto the PVK layer at a rate of less than 0.1 angstrom/second. The thickness of the 6P layer is 400-800 angstroms. The PPyVPV layer was subsequently spin coated over the 6P from xylenes solution ~2500 rpm. All the spin coating procedures were carried out inside a class 100 cleanroom. The top metal electrode (Al) was deposited by vacuum evaporation at a pressure below 10^{-6} torr. To prevent damage to the polymers, the substrate was mounted on a cold-water cooled surface during evaporation. Photoluminescence (PL) and electroluminescence (EL) were measured using a PTI fluorometer (model QM-1). The current-voltage (I-V) characteristics were measured simultaneously with EL using two Keithley model 195A multimeters while the dc voltage was applied by a HP model 6218A DC power supply. Quantum efficiency and brightness were measured using a calibrated photodiode (UDT UV100).

Example 1 - ITO/6P/PPy/Al

Figure 3 shows the EL spectra of a bilayer device ITO/6P/PPy/Al operated under different applied voltages. Under low voltages, the EL spectra show two peaks at 425 nm and 450 nm, in addition to shoulders at 400 nm and 480 nm. The bilayer EL spectrum can be roughly represented by a superposition of the two individual 6P and PPy EL spectra, suggesting that the light is generated near the interface between 6P and PPy. The EL appears light blue to the eye. As the voltage increases, a peak at 565 nm appears and eventually becomes dominant. The current-voltage characteristics of such devices are shown in Figure 4.

Example 2 - ITO/PVK/6P/PPy/Al

Figure 5(a) shows EL spectra of a three layer device ITO/PVK/6P/PPy/Al. At low applied voltages, the EL spectrum is very similar to that of the bilayer device, which is light blue in color. The CIE chromaticity x,y coordinates of the EL spectra at 17 V is calculated to be (0.237,0.224). As voltage increases, the peak at 450 nm grows. At the same time, a new peak at ~ 605 nm appears and grows, which driving the location of the EL spectra in the CIE diagram towards white along a straight line, as shown in Figure 6 inset. At 27 V, the emitted light appears bright white to the eye. The CIE chromaticity x,y coordinates of the spectra at 27 V is calculated to be (0.322,0.315). Below 27 V, the voltage dependent EL spectra are more or less reversible. Above 27 V, the device went through an irreversible change. The features at the blue region disappears and the EL spectrum is dominated by a broad peak at 605 nm. The light appears greenish white to the eye and its CIE chromaticity x,y coordinates is calculated to be (0.400,0.411). It is noted that the EL spectra do not change with applied voltages above 27 V although its brightness increases with increasing applied voltages.

A modest quantum efficiency and brightness were achieved for the bilayer devices. The incorporation of hole transporting layer PVK in the three layer device significantly improved the device performance. Figure 6 shows the typical current-voltage (I-V) and luminance-voltage characteristics of the three layer devices. The devices have a typical turn on voltage of ~15-17 V. After turn on, the light intensity roughly followed the current density. The discrepancy between them is probably due to the spectral change with the applied voltages. The maximum brightness is well above 100 cd/m^2 when the EL spectra at 27 V is used to calculate the brightness. The

quantum efficiency of above 0.1% has been achieved for the initial unoptimized three layer devices.

Example 3 - ITO/PPyVPV/6P/Al

Figure 7 shows the EL spectra of a bilayer device ITO/PPyVPV/6P/Al operated under different applied voltages. Under low voltages (~ 10 V), the EL spectra show a main peak at ~620 nm, in addition to three weak peaks from 6P. As the voltage increases, the features from 6P increase and becomes dominant above 14 V. The current-voltage characteristics of such devices are shown in Figure 8.

Example 4 - ITO/PVK/PPyVPV/6P/Al

Figure 9 shows EL spectra of a three layer device ITO/PVK/PPyVPV/6P/Al. Similar phenomena are observed as the bilayer device without PVK, except that the higher wavelength peak now is further shifted to ~680 nm, and the EL spectra are more dominated by the 6P emission. The incorporation of hole transporting layer PVK in the three layer device significantly improved the device efficiency (> 0.1%) and brightness (> 100 cd/m^2). Figure 10 shows the typical current-voltage (I-V) characteristics of the three layer devices.

Example 5 - ITO/PPyVPV/6P/PPy/Al

Figure 11 shows the EL spectra of a three layer device ITO/PPyVPV/6P/PPy/Al operated under different applied voltages. The EL spectra show three main features: three peaks from 6P below 450 nm, a peak at ~530 nm, and a peak at ~700 nm. Under low voltages, the EL spectra are dominated by the features below 450 nm and 700 nm. As the voltage increases, the peak at

530 nm grows and eventually becomes dominant. The current-voltage characteristics of such devices are shown in Figure 12.

Example 6 - ITO/6P/PPyVPV/Al

Figure 13 and Figure 14 shows the EL spectra and current-voltage characteristics, respectively, of a bilayer device ITO/6P/PPyVPV/Al operated under different applied voltages. The phenomena are very similar to Example 3.

Example 7 - ITO/PVK/6P/PPyVPV/Al

Figure 15 shows EL spectra of a three layer device ITO/PVK/6P/PPyVPV/Al. The EL spectra show three main features: three peaks from 6P below 450 nm and two peaks at 540 nm and 600 nm. The strength of the three features changes as the applied voltage changes. It is noted that the relative strength of the three features is strongly influenced by the thickness of the 6P layer. For relatively thick (~ 800 nm) 6P, the three peaks below 450 nm dominate. For relative thin (~ 400 nm) 6P layer, the peaks at 540-600 nm dominate. As compare to the bilayer device without PVK, the three layer device with PVK shows significantly improved quantum efficiency and brightness. Figure 16 shows the typical current-voltage (I-V) and luminance-voltage characteristics of the three layer devices. The devices have a typical turn on voltage of ~15 V. After turn on, the light intensity roughly followed the current density. The maximum brightness is well above 300 cd/m^2. The quantum efficiency of above 0.5% has been achieved for the initial unoptimized three layer devices.

Example 8 - ITO/PVK/6P/Al

Figure 17 and Figure 18 show the EL spectra and current-voltage characteristics, and luminance-voltage respectively, of a bilayer device ITO/PVK/6P/Al. The EL spectra of the bilayer device are very similar to those of the single layer ITO/6P/Al device, and show modest, but not visually significant, change with applied voltage. However the brightness and quantum efficiency of the bilayer device increase at least two orders of magnitude than those of the single layer device, reaching ~600 cd/m^2 and 1-2%, respectively, for the unoptimized bilayer device.

The preferred embodiments herein disclosed are not intended to be exhaustive or to unnecessarily limit the scope of the invention. The preferred embodiments were chosen and described in order to explain the principles of the present invention so that others skilled in the art may practice the invention. Having shown and described preferred embodiments of the present invention, it will be within the ability of one of ordinary skill in the art to make alterations or modifications to the present invention, such as through the substitution of equivalent materials or structural arrangements, so as to be able to practice the present invention without departing from its spirit as reflected in the appended claims. It is the intention, therefore, to limit the invention only as indicated by the scope of the claims, the text of which is incorporated herein by reference.

What is claimed is:

1. A color variable electroluminescent device comprising:

(a) a polymeric first layer adapted to act as a light-emitting layer, said polymeric first layer capable of conducting a current;

(b) a second layer adapted to act as a light-emitting layer and comprising a material capable of conducting a current and selected from the group consisting of molecular and oligomeric electroluminescent materials, said polymeric first layer being in electrical contact with said second layer; and

(c) electrodes respectively in electrical contact said polymeric first layer and said second layer,

whereby said device is capable of producing a color-variable light emission upon a variation in the voltage of the current being conducted through said device.

2. A color variable electroluminescent device according to claim 1 wherein said polymeric first layer comprises a blend of polymers selected from the group consisting of conjugated polymers, copolymers, and mixtures thereof.

3. A color variable electroluminescent device according to claim 1 wherein said polymeric first layer comprises a polymer selected from the group consisting of poly(pyridyl vinylene phenylene vinylene)s, polyvinylcarbazoles, polypyridine polypyridines, polypyridylvinylenes, polythiophenes, polyphenylenes, polyphenylenevinylenes, polyphenylenebenzobisthiozoles, polyfluorenes, polyvinylcarbazoles, polyacetylenes and polythienylenevinylenes.

4. A color variable electroluminescent device according to claim 1 wherein said second layer comprises a material selected from the group consisting of parapentaphenyl, parasexiphenyl, pentathiophene, sexithiophene septathiophene, oligomers of stilbene and oligomers of bipyridine.

5. A color variable electroluminescent device according to claim 1 wherein said second layer comprises a material selected from the group consisting of quinacridone, stilbene, rubrene, 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran, and 8-hydroxyquinone.

6. A color variable electroluminescent device according to claim 1 wherein one of said electrodes comprises indium tin oxide (ITO), gold and doped conjugated polymers.

7. A color variable electroluminescent device according to claim 6 wherein one of said electrodes comprises a doped conjugated polymers is selected from the group consisting of such as doped polyaniline, doped polypyrrole and doped polythiophenes, and derivatives thereof.

8. A color variable electroluminescent device according to claim 1 wherein one of said electrodes comprises a material selected from the group consisting of aluminum, calcium, magnesium-silver and lithium -aluminum.

9. A color variable electroluminescent device according to claim 1 additionally comprising a source of a direct electric current supplied to said electrodes.

10. A color variable electroluminescent device according to claim 1 additionally comprising a source of an alternating electric current supplied to said electrodes.

11. A color variable electroluminescent device according to claim 1 wherein said device is disposed on a substrate material.

12. A color variable electroluminescent device according to claim 11 wherein said substrate material is selected from the group consisting of glass and insulating plastic.

13. A color-variable electroluminescent device comprising:

(a) a first layer of a material adapted to act as a light-emitting layer and capable of conducting a current;

(b) a second layer of a material adapted to act as a light-emitting layer and capable of conducting a current; and

(c) an intermediate layer adapted to act as a light emitting layer and capable of conducting a current, said intermediate disposed in electrical contact between said first layer and said second layer;

wherein two of said layers independently comprise a polymeric material adapted to act as a light-emitting layer and capable of conducting a current, and the other of said layers comprising a material adapted to act as a light-emitting layer, capable of conducting a current and selected from the group consisting of molecular and oligomeric electroluminescent materials; and

(d) two electrodes in electrical contact respectively with said first layer and said second layer,

whereby said device is capable of producing a color-variable light emission upon a variation in the voltage of the current being conducted through said device.

14. A color variable electroluminescent device according to claim 13 wherein said polymeric material comprises a blend of polymers selected from the group consisting of conjugated polymers, copolymers, and mixtures thereof.

15. A color variable electroluminescent device according to claim 13 wherein said polymeric material comprises a polymer selected from the group consisting of polypyridyl vinylene phenylene vinylenes, polyvinylcarbazoles, polypyridine polypyridines, polypyridylvinylenes, polythiophenes, polyphenylenes, polyphenylenevinylenes, polyphenylenebenzobisthiozoles, polyfluorenes, polyvinylcarbazoles, polyacetylenes and polythienylenevinylenes.

16. A color variable electroluminescent device according to claim 13 wherein said second layer comprises a material selected from the group consisting of parapentaphenyl, parasexiphenyl, pentathiophene, sexithiophene septathiophene, oligomers of stilbene and oligomers of bipyridine.

17. A color variable electroluminescent device according to claim 13 wherein said second layer comprises a material selected from the group consisting of quinacridone, stilbene, rubrene, 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran, and 8-hydroxyquinone.

18. A color variable electroluminescent device according to claim 13 wherein one of said electrodes comprises indium tin oxide (ITO), gold and doped conjugated polymers.

19. A color variable electroluminescent device according to claim 18 wherein one of said electrodes comprises a doped conjugated polymers is selected from the group consisting of such as doped polyaniline, doped polypyrrole and doped polythiophenes, and derivatives thereof.

20. A color variable electroluminescent device according to claim 13 wherein one of said electrodes comprises a material selected from the group consisting of aluminum, calcium, magnesium-silver and lithium -aluminum.

21. A color variable electroluminescent device according to claim 13 additionally comprising a source of a direct electric current supplied to said electrodes.

22. A color variable electroluminescent device according to claim 13 additionally comprising a source of an alternating electric current supplied to said electrodes.

23. A color variable electroluminescent device according to claim 13 wherein said device is disposed on a substrate material.

24. A color variable electroluminescent device according to claim 23 wherein said substrate material is selected from the group consisting of glass and insulating plastic.

25. A color-variable electroluminescent device comprising:

(a) a first layer of a material adapted to act as a light-emitting layer and capable of conducting a current;

(b) a second layer of a material adapted to act as a light-emitting layer and capable of conducting a current; and

(c) an intermediate layer adapted to act as a light emitting layer and capable of conducting a current, said intermediate disposed in electrical contact between said first layer and said second layer;

wherein two of said layers independently comprise a material adapted to act as a light-emitting layer, capable of conducting a current and selected from the group consisting of molecular and

oligomeric electroluminescent materials, and the other of said layers comprising a polymeric material adapted to act as a light-emitting layer and capable of conducting a current; and

(d) two electrodes in electrical contact respectively with said first layer and said second layer,

whereby said device is capable of producing a color-variable light emission upon a variation in the voltage of the current being conducted through said device.

26. A color variable electroluminescent device according to claim 25 wherein said polymeric material comprises a blend of polymers selected from the group consisting of conjugated polymers, copolymers, and mixtures thereof.

27. A color variable electroluminescent device according to claim 25 wherein said polymeric material comprises a polymer selected from the group consisting of polypyridyl vinylene phenylene vinylenes, polyvinylcarbazoles, polypyridine polypyridines, polypyridylvinylenes, polythiophenes, polyphenylenes, polyphenylenevinylenes, polyphenylenebenzobisthiozoles, poly-fluorenes, polyvinylcarbazoles, polyacetylenes and polythienylenevinylenes.

28. A color variable electroluminescent device according to claim 25 wherein said second layer comprises a material selected from the group consisting of parapentaphenyl, parasexiphenyl, pentathiophene, sexithiophene septathiophene, oligomers of stilbene and oligomers of bipyridine.

29. A color variable electroluminescent device according to claim 25 wherein said second layer comprises a material selected from the group consisting of quinacridone, stilbene, rubrene, 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran, and 8-hydroxyquinone.

30. A color variable electroluminescent device according to claim 25 wherein one of said electrodes comprises indium tin oxide (ITO), gold and doped conjugated polymers.

31. A color variable electroluminescent device according to claim 30 wherein one of said electrodes comprises a doped conjugated polymers is selected from the group consisting of such as doped polyaniline, doped polypyrrole and doped polythiophenes, and derivatives thereof.

32. A color variable electroluminescent device according to claim 25 wherein one of said electrodes comprises a material selected from the group consisting of aluminum, calcium, magnesium-silver and lithium -aluminum.

33. A color variable electroluminescent device according to claim 25 additionally comprising a source of a direct electric current supplied to said electrodes.

34. A color variable electroluminescent device according to claim 25 additionally comprising a source of an alternating electric current supplied to said electrodes.

35. A color variable electroluminescent device according to claim 25 wherein said device is disposed on a substrate material.

36. A color variable electroluminescent device according to claim 35 wherein said substrate material is selected from the group consisting of glass and insulating plastic.

37. A method of producing a color-variable light from an electroluminescent device, said method comprising the steps:

(1) obtaining a color variable electroluminescent device comprising:

(a) a polymeric first layer adapted to act as a light-emitting layer, said polymeric first layer capable of conducting a current;

(b) a second layer adapted to act as a light-emitting layer and comprising a material capable of conducting a current and selected from the group consisting of molecular and oligomeric electroluminescent materials, said polymeric first layer being in electrical contact with said second layer; and

(c) electrodes respectively in electrical contact said polymeric first layer and said second layer,

whereby said device is capable of producing a color-variable light emission upon a variation in the voltage of the current being conducted through said device; and

(2) causing sufficient current to flow into said device so as to cause said device to emit light, and varying the voltage of said current to a sufficient degree so as to cause a variation in the color of said light.

38. A method of producing a color-variable light from an electroluminescent device, said method comprising the steps:

(1) obtaining a color variable electroluminescent device comprising:

(a) a first layer of a material adapted to act as a light-emitting layer and capable of conducting a current;

(b) a second layer of a material adapted to act as a light-emitting layer and capable of conducting a current; and

(c) an intermediate layer adapted to act as a light emitting layer and capable of conducting a current, said intermediate disposed in electrical contact between said first layer and said second layer;

wherein two of said layers independently comprise a polymeric material adapted to act as a light-emitting layer and capable of conducting a current, and the other of said layers comprising a material adapted to act as a light-emitting layer, capable of conducting a current and selected from the group consisting of molecular and oligomeric electroluminescent materials; and

(d) two electrodes in electrical contact respectively with said first layer and said second layer,

whereby said device is capable of producing a color-variable light emission upon a variation in the voltage of the current being conducted through said device; and

(2) causing sufficient current to flow into said device so as to cause said device to emit light, and varying the voltage of said current to a sufficient degree so as to cause a variation in the color of said light.

39. A method of producing a color-variable light from an electroluminescent device, said method comprising the steps:

(1) obtaining a color variable electroluminescent device comprising:

(a) a first layer of a material adapted to act as a light-emitting layer and capable of conducting a current;

(b) a second layer of a material adapted to act as a light-emitting layer and capable of conducting a current; and

(c) an intermediate layer adapted to act as a light emitting layer and capable of conducting a current, said intermediate disposed in electrical contact between said first layer and said second layer;

wherein two of said layers independently comprise a material adapted to act as a light-emitting layer, capable of conducting a current and selected from the group consisting of molecular and oligomeric electroluminescent materials, and the other of said layers comprising a polymeric material adapted to act as a light-emitting layer and capable of conducting a current; and

(d) two electrodes in electrical contact respectively with said first layer and said second layer,

whereby said device is capable of producing a color-variable light emission upon a variation in the voltage of the current being conducted through said device; and

(2) causing sufficient current to flow into said device so as to cause said device to emit light, and varying the voltage of said current to a sufficient degree so as to cause a variation in the color of said light.

40. An electroluminescent device comprising:

(a) a polymeric first layer adapted to act as a light-emitting layer, said polymeric first layer capable of conducting a current and comprising polyvinylcarbazole;

(b) a second layer adapted to act as a light-emitting layer and comprising a material capable of conducting a current, said material comprising parasexiphenyl, said polymeric first layer being in electrical contact with said second layer; and

(c) electrodes respectively in electrical contact with said polymeric first layer and said second layer.

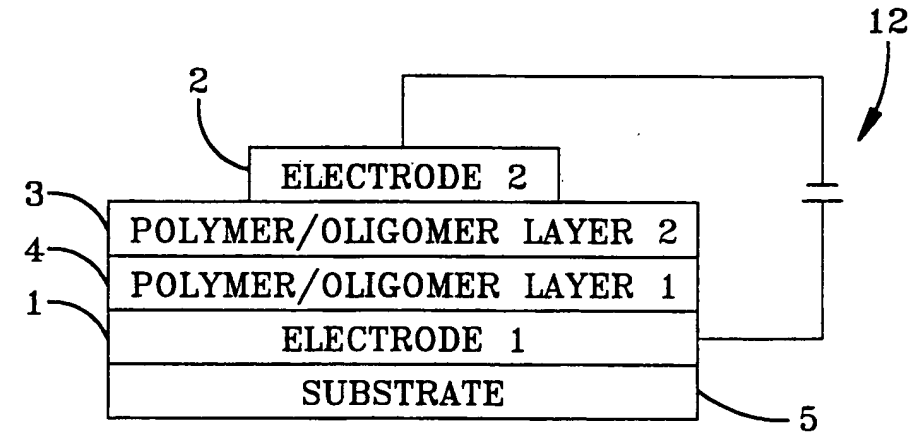


FIG-1a

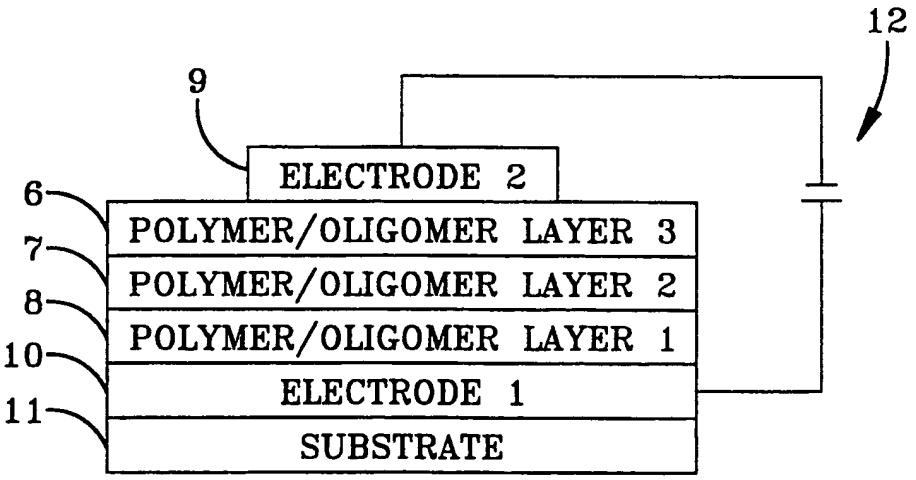
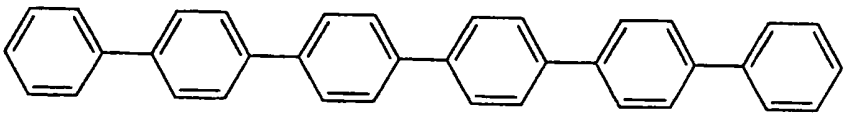
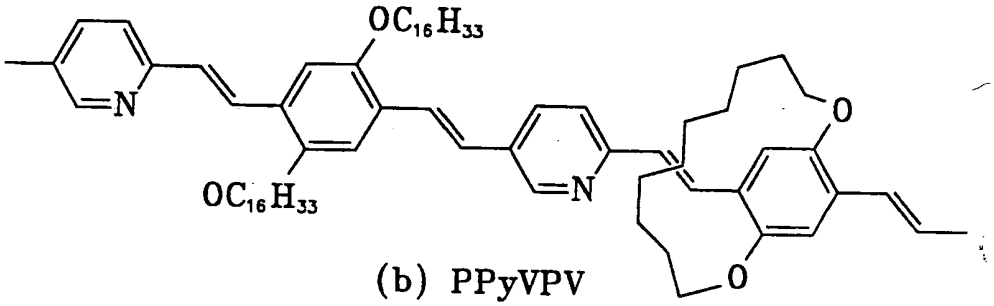


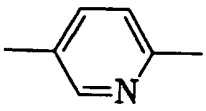
FIG-1b



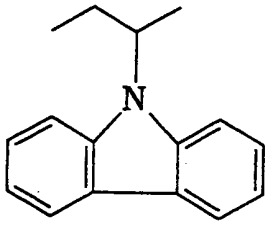
(a) 6P



(b) PPyVPV



(c) PPy



(d) PVK

FIG-2

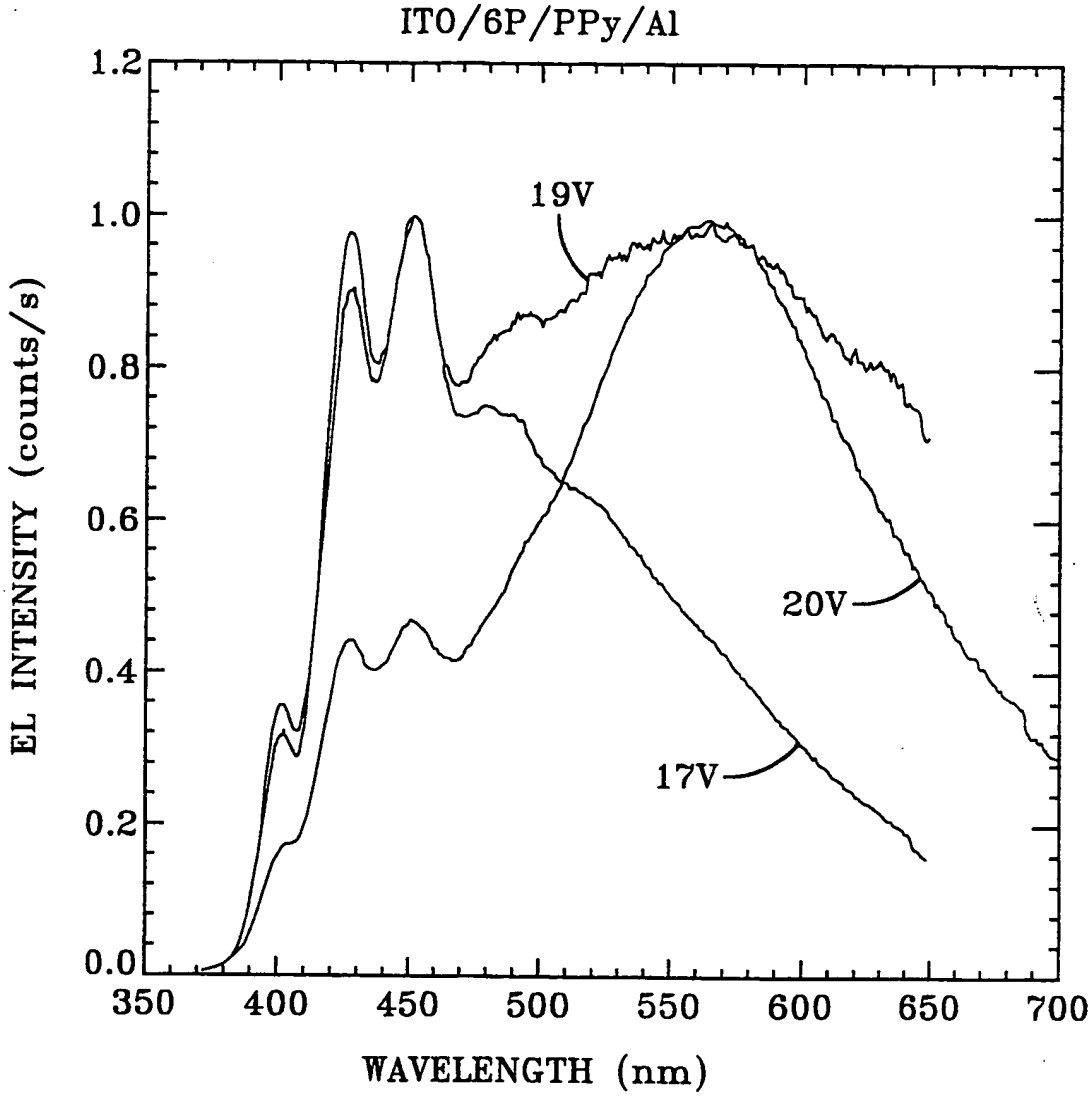
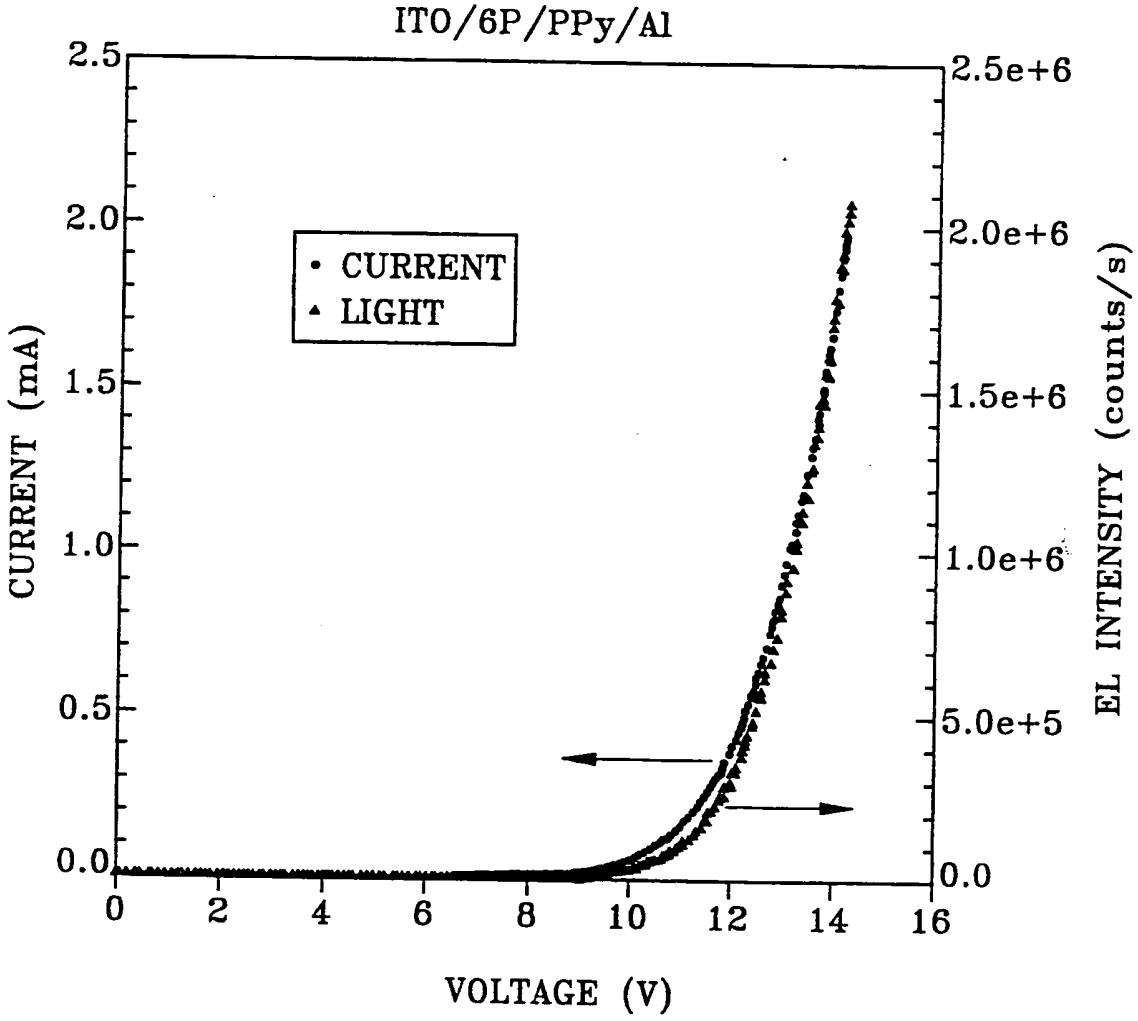


FIG-3



FIG–4

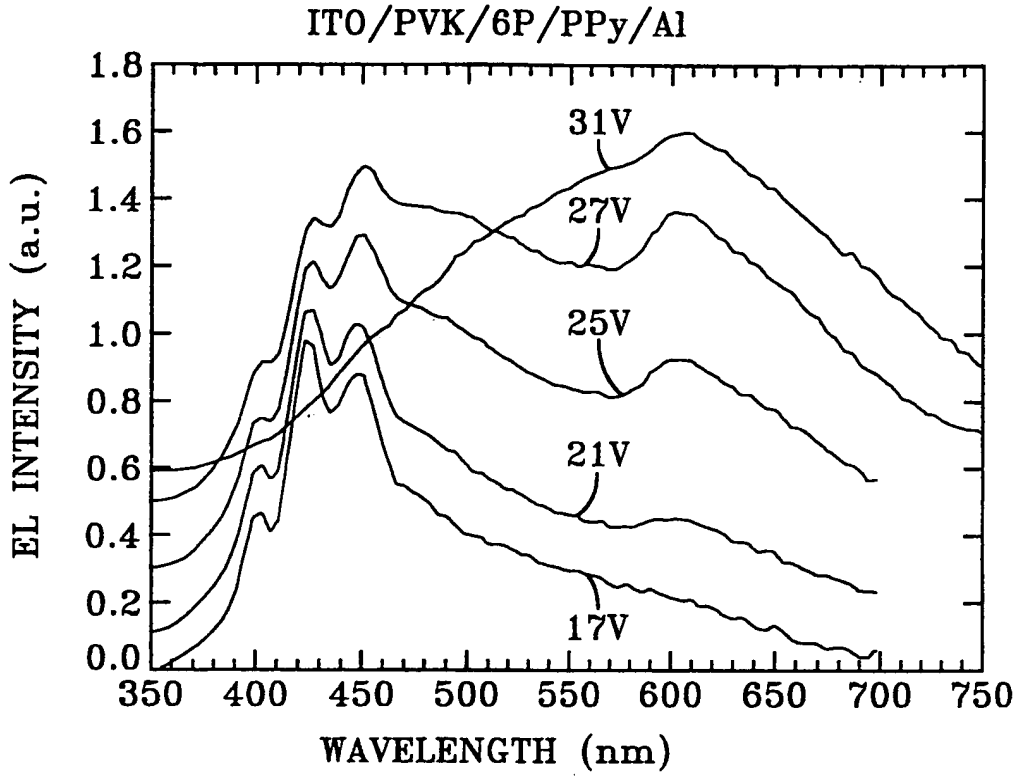


FIG-5a

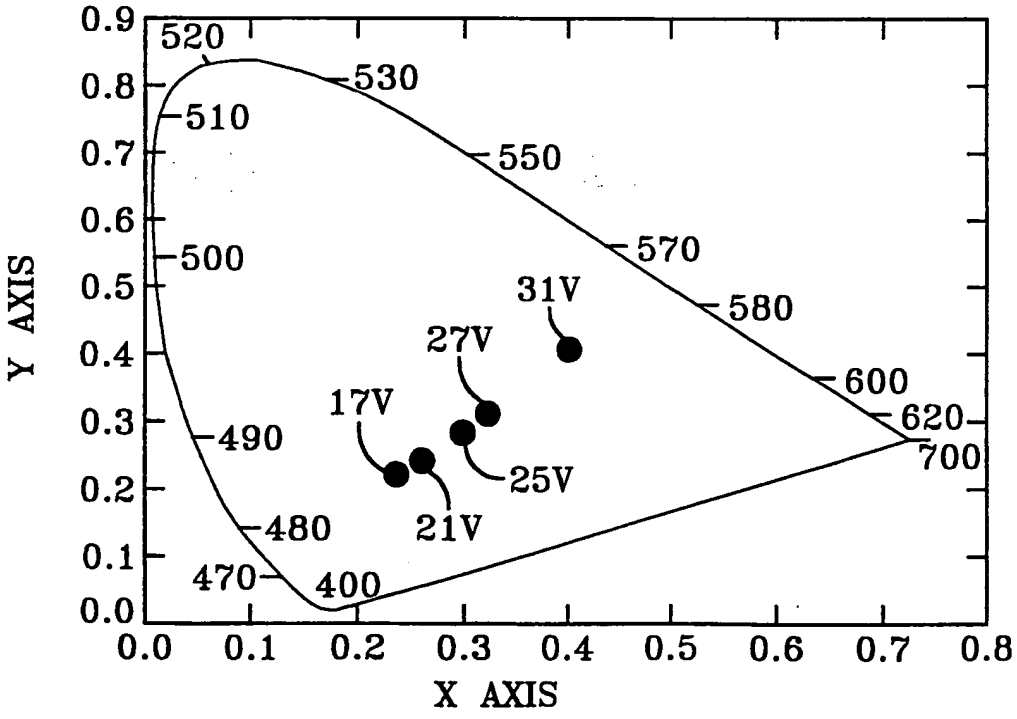


FIG-5b

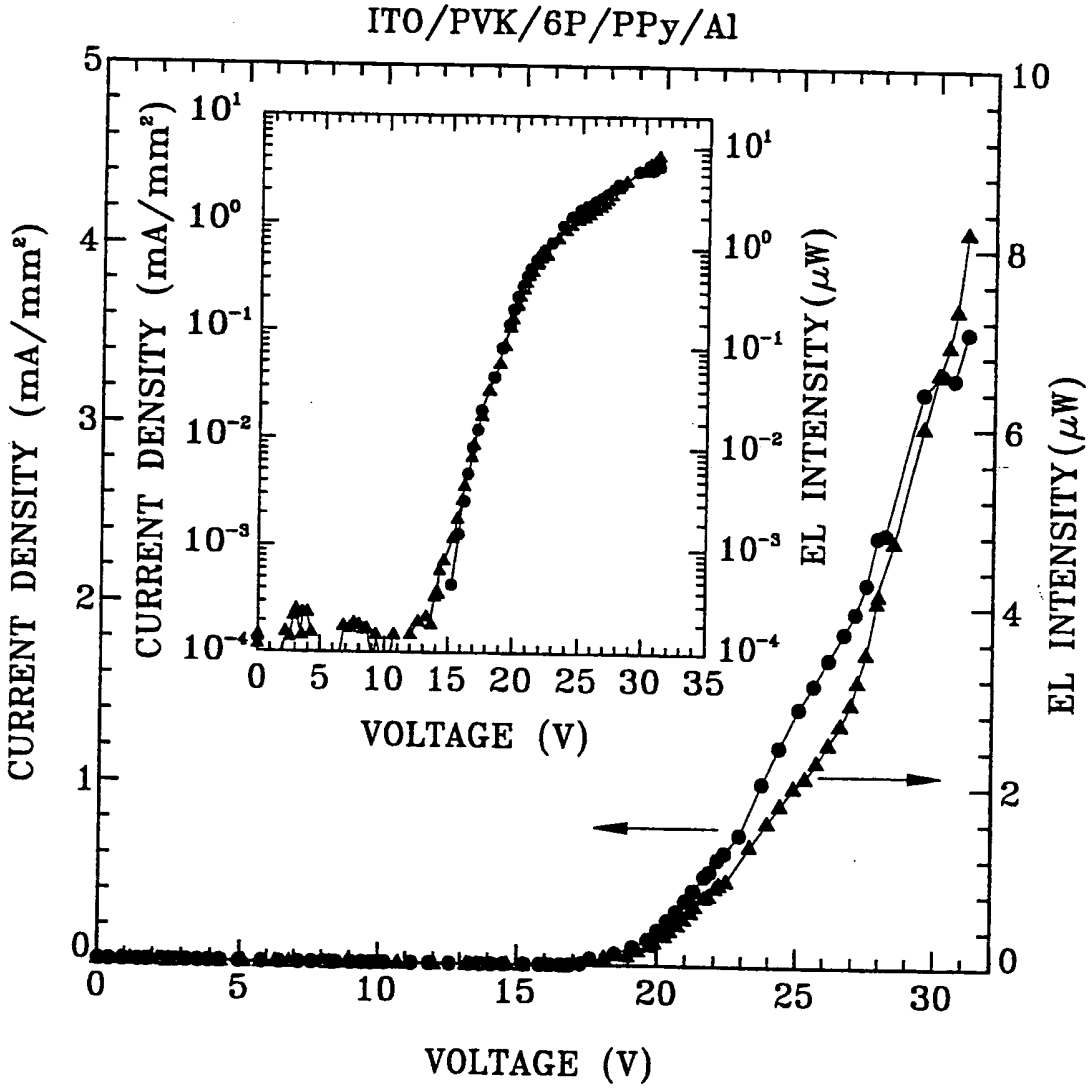


FIG-6

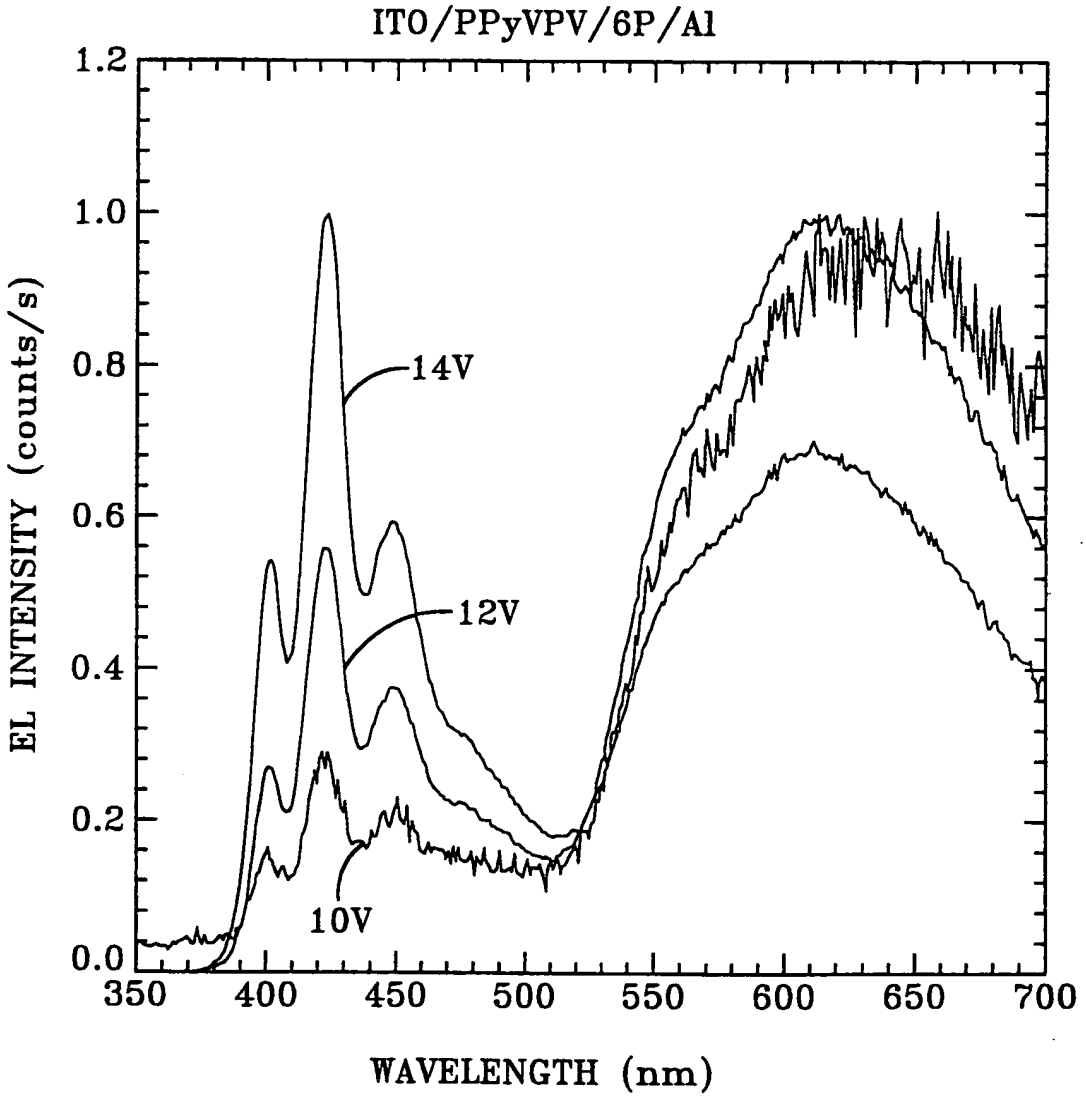


FIG-7

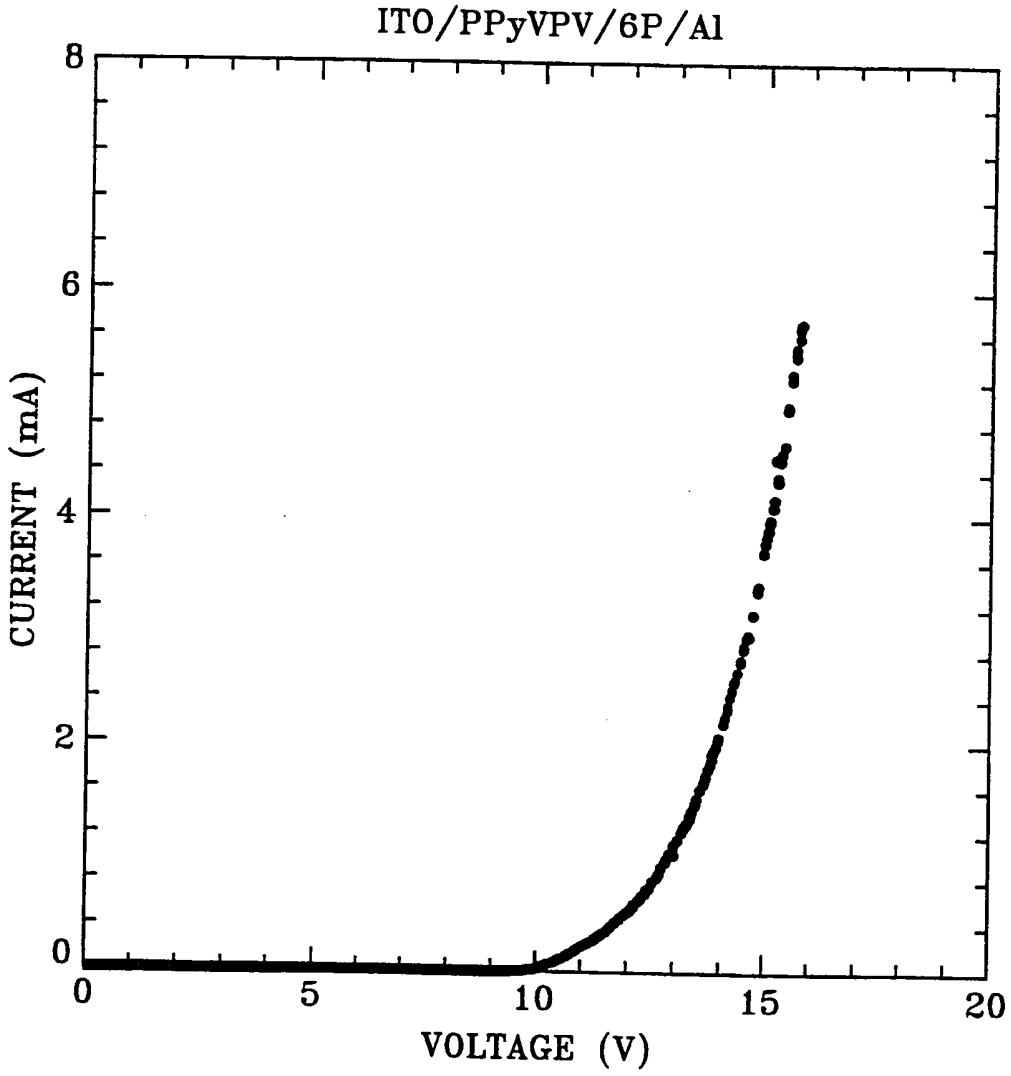


FIG-8

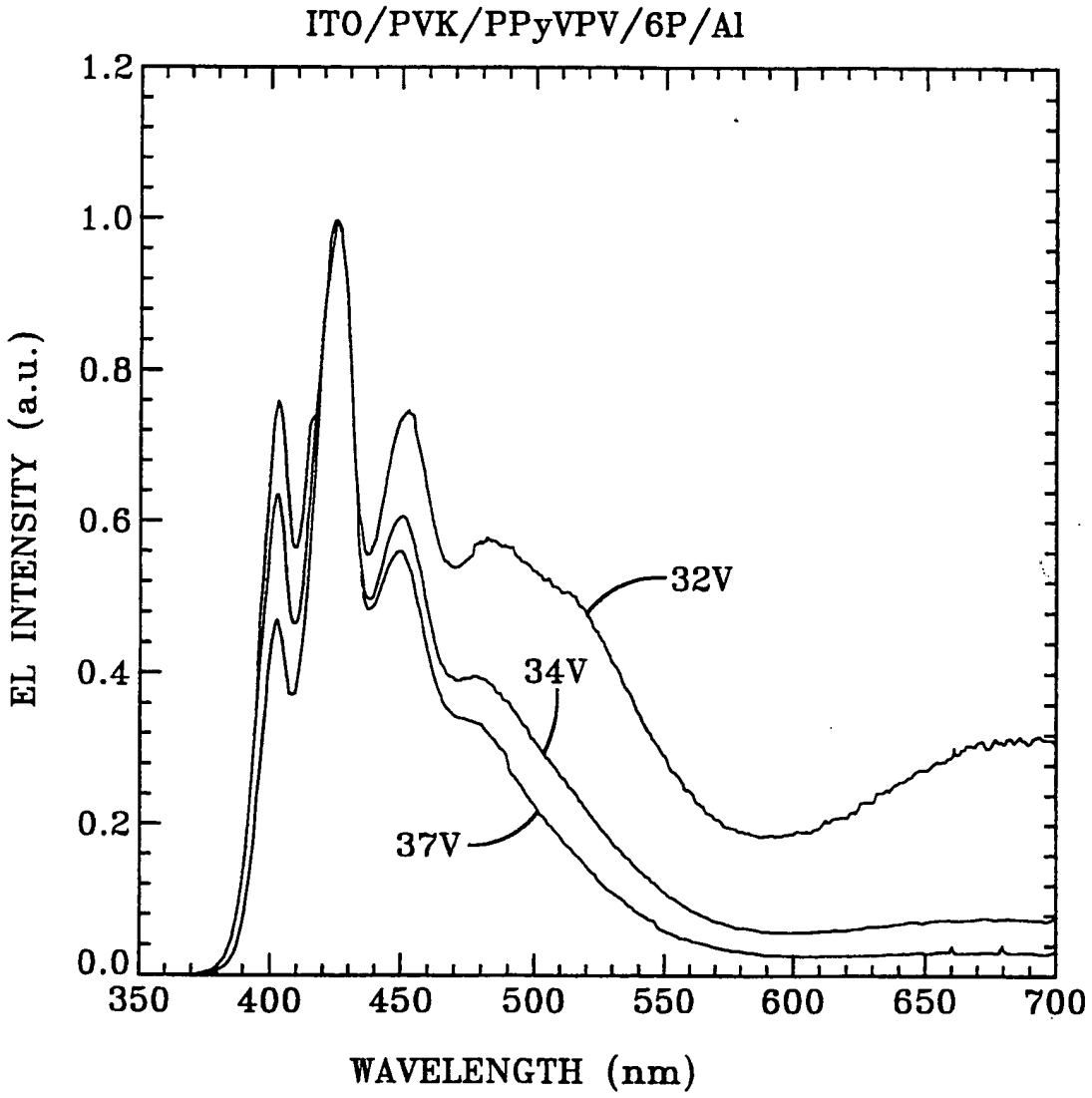


FIG-9

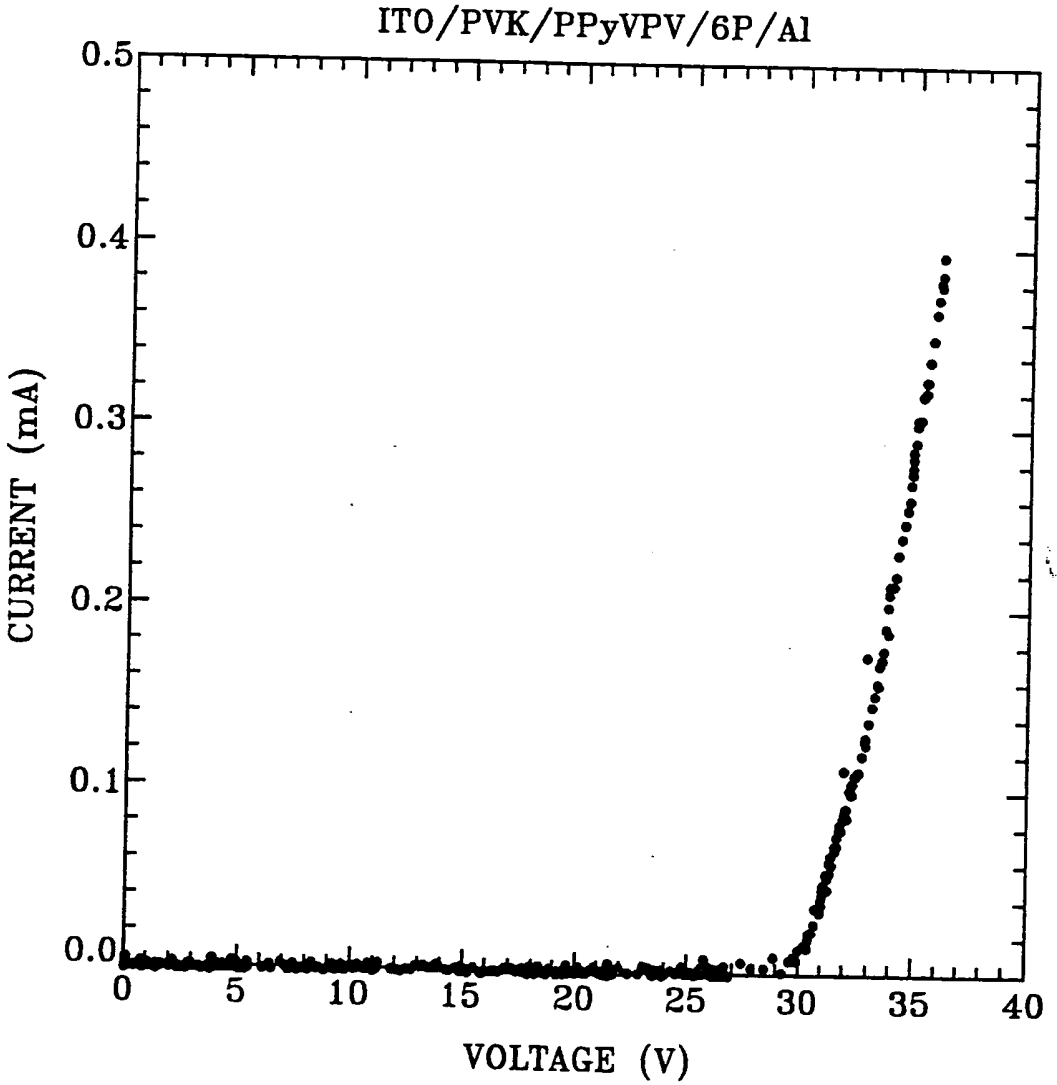


FIG-10

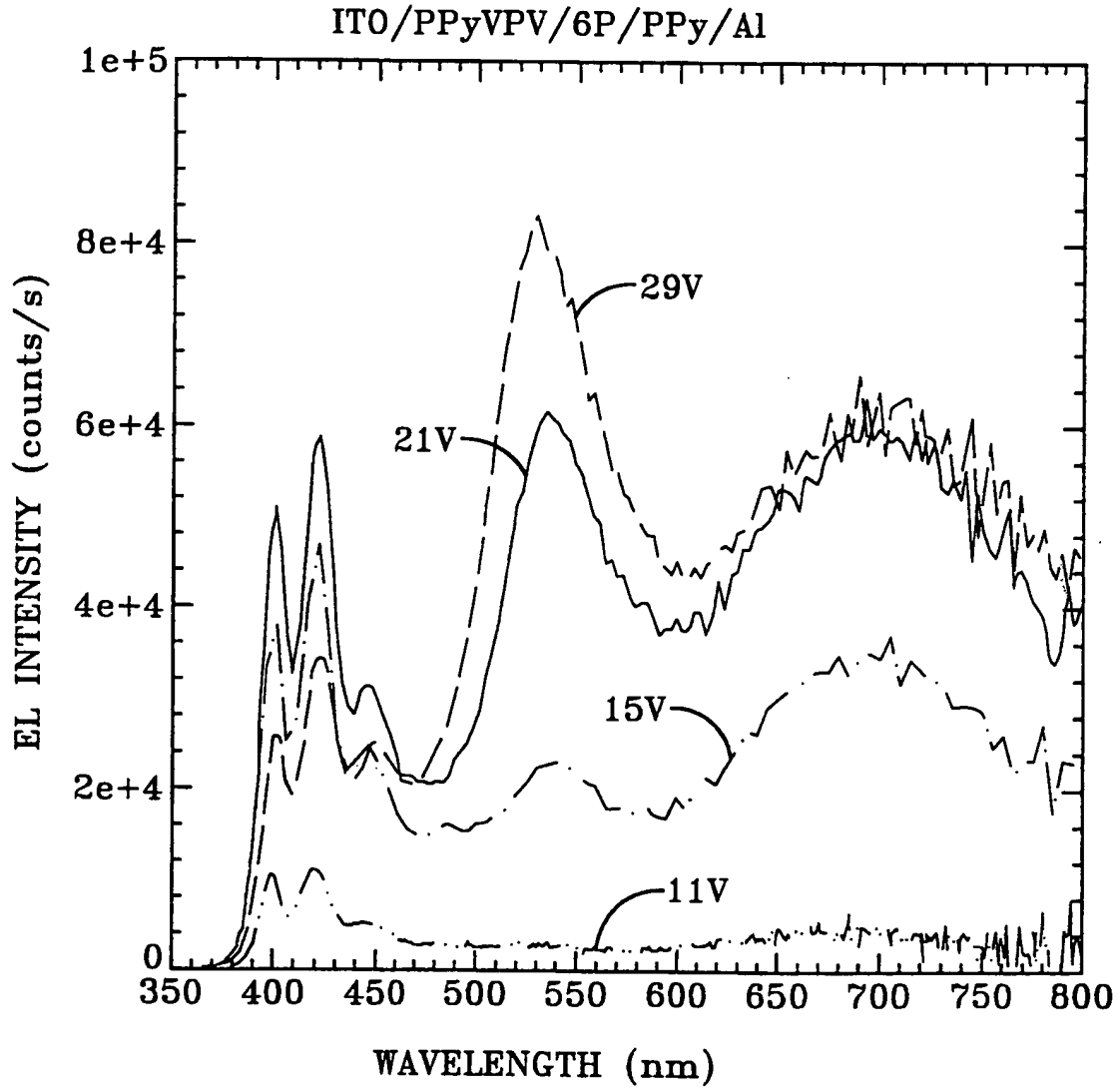


FIG-11

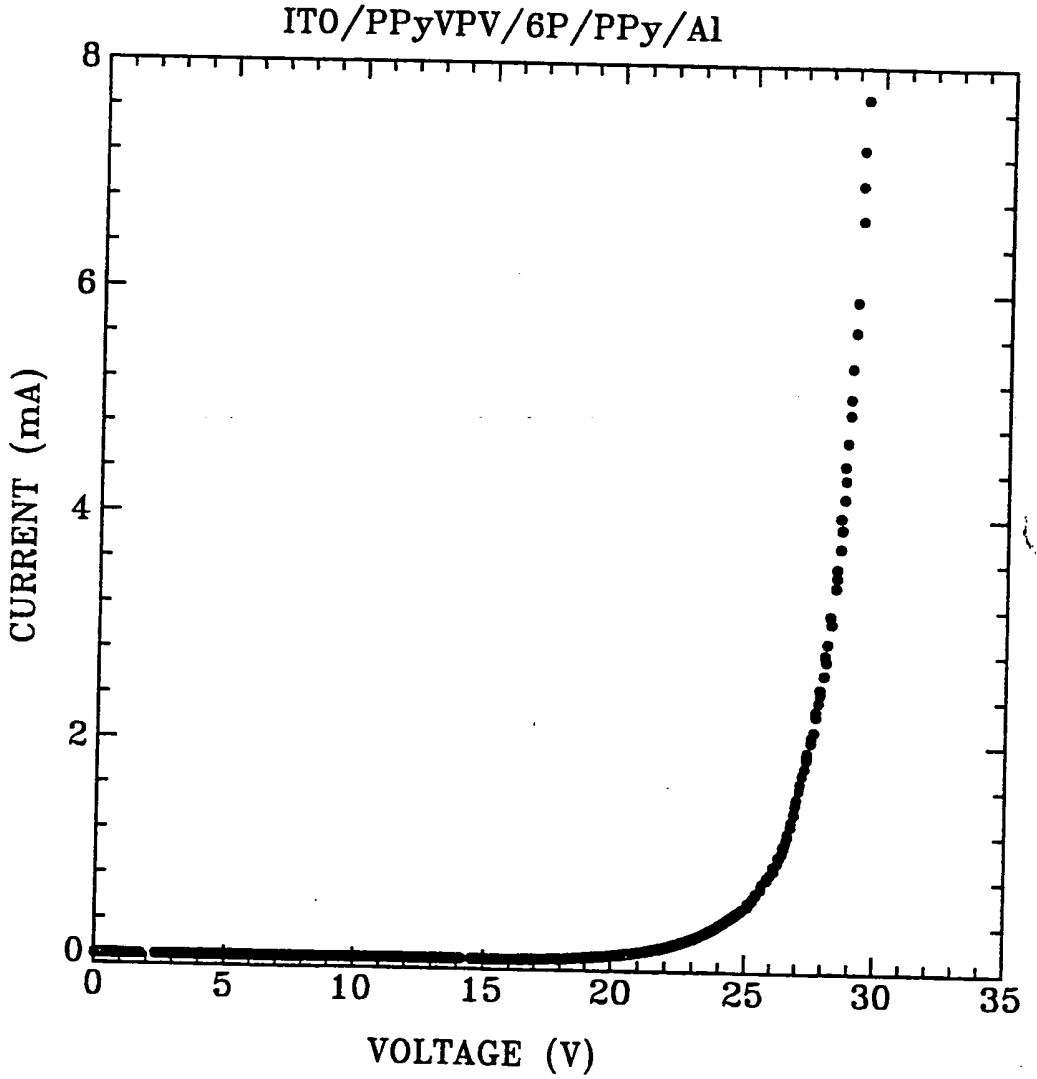


FIG-12

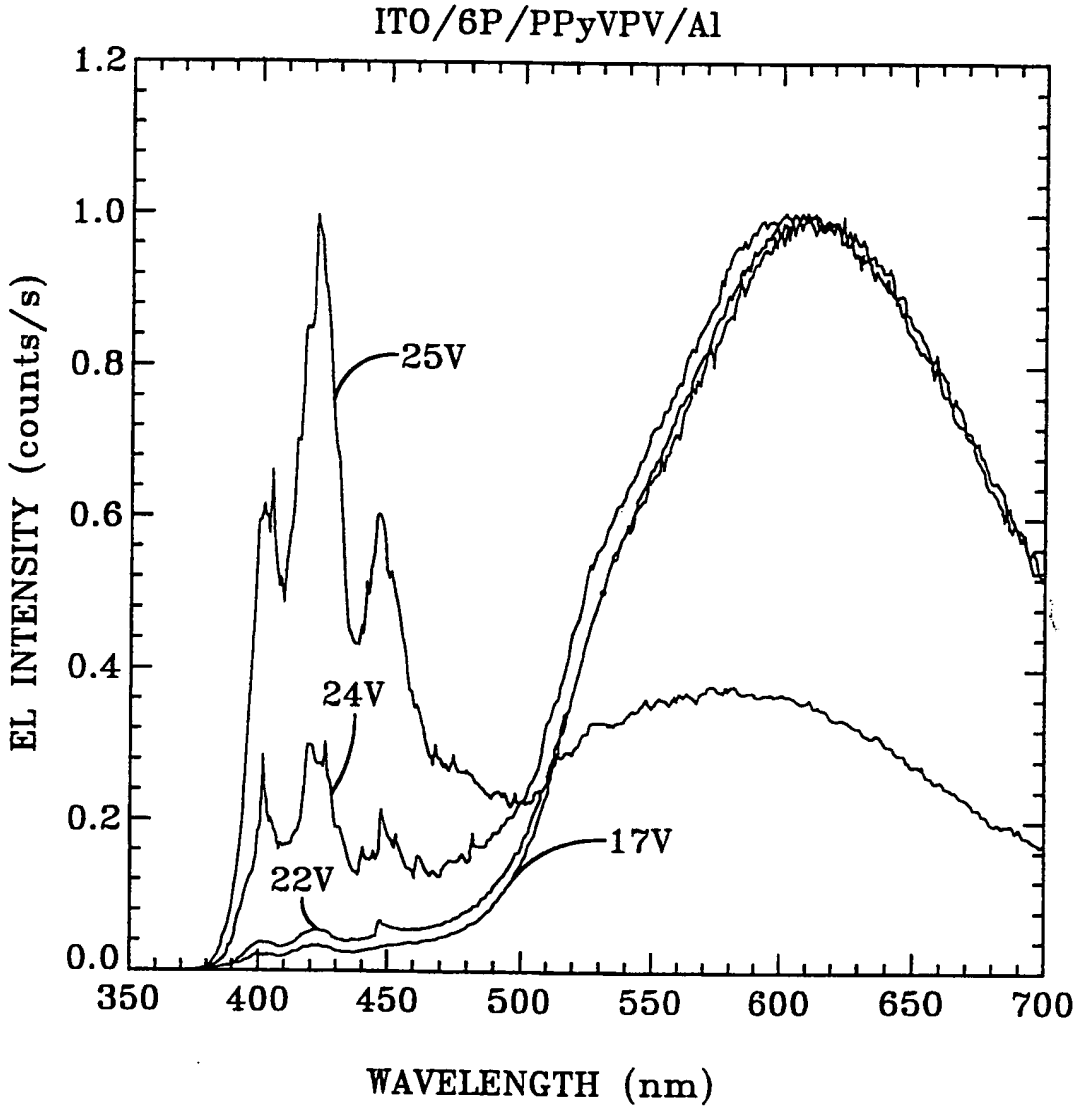


FIG-13

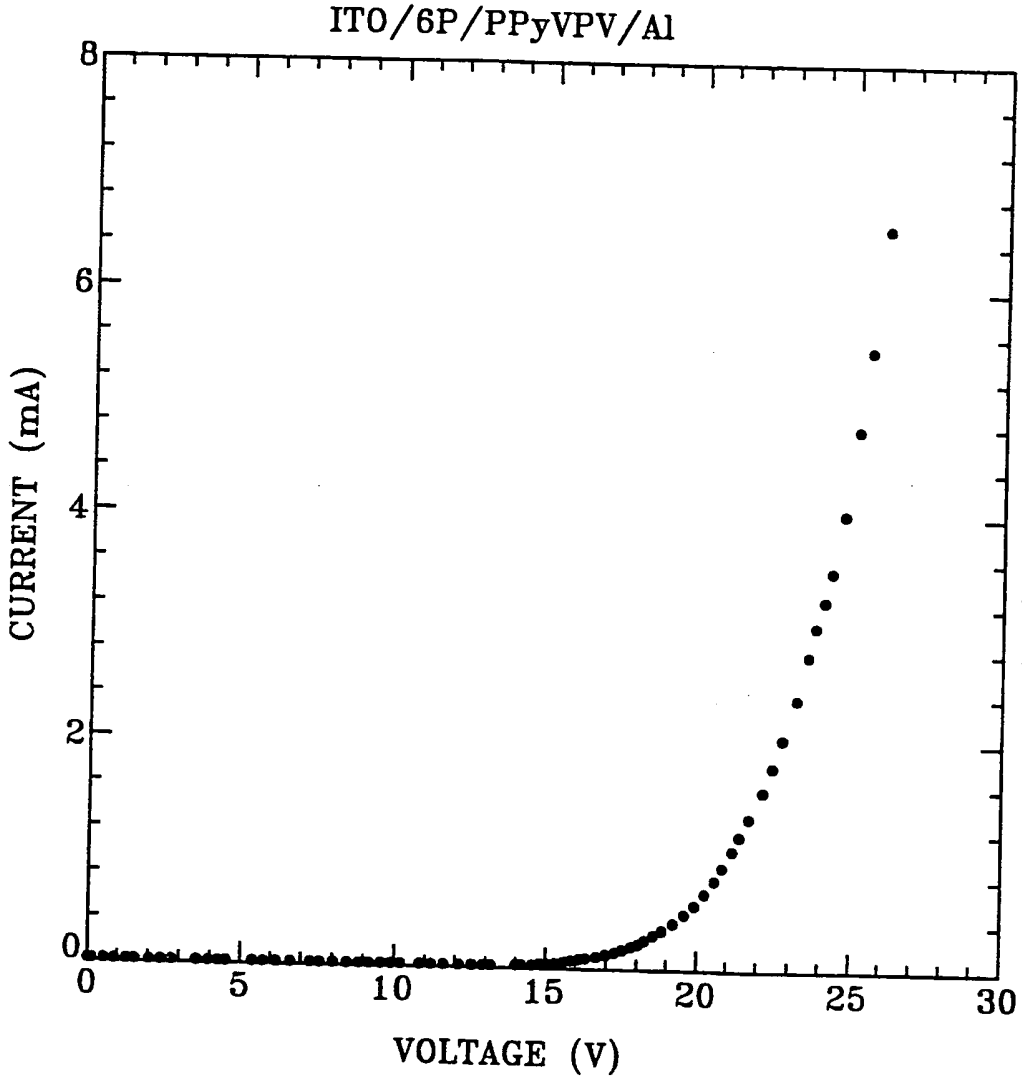


FIG-14

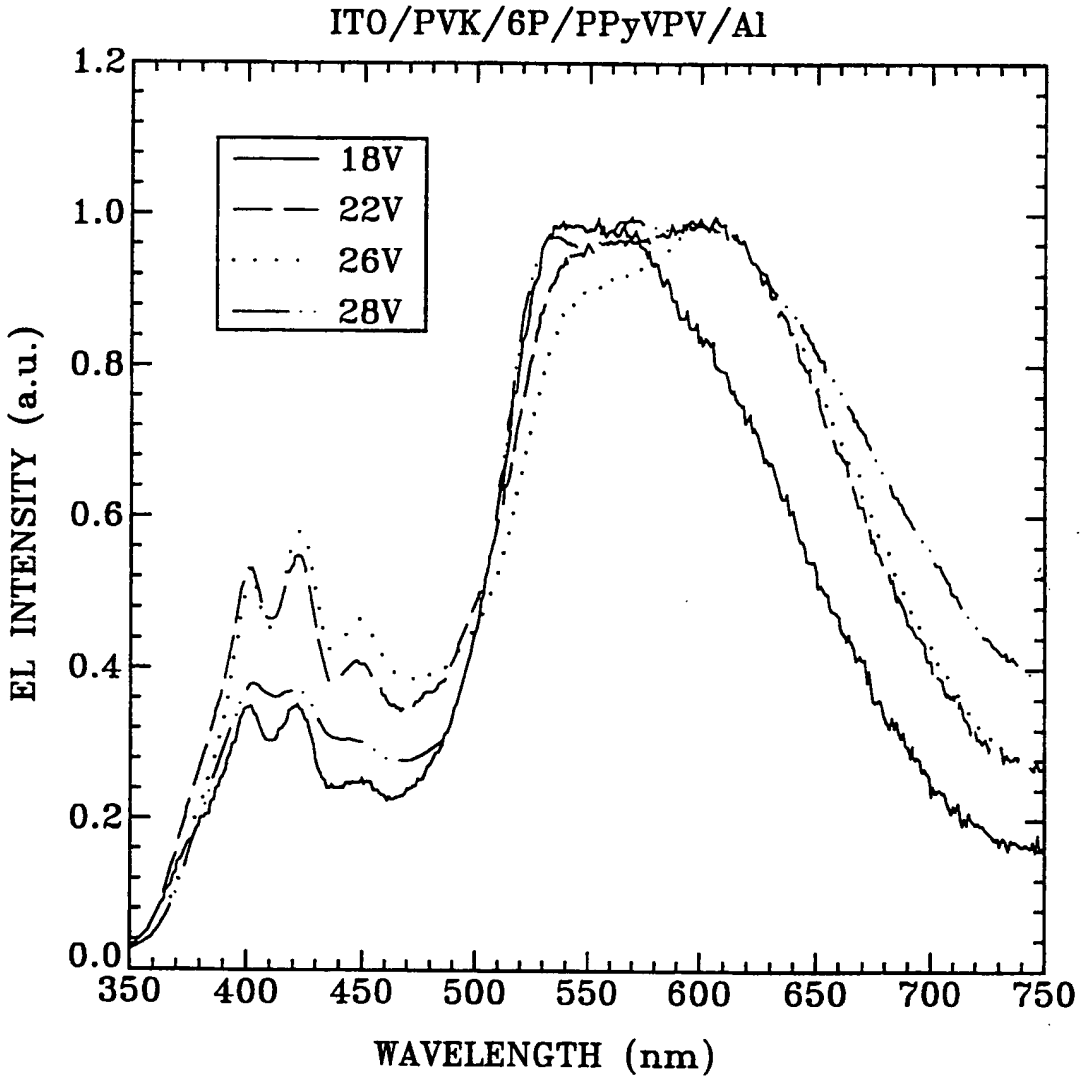


FIG-15

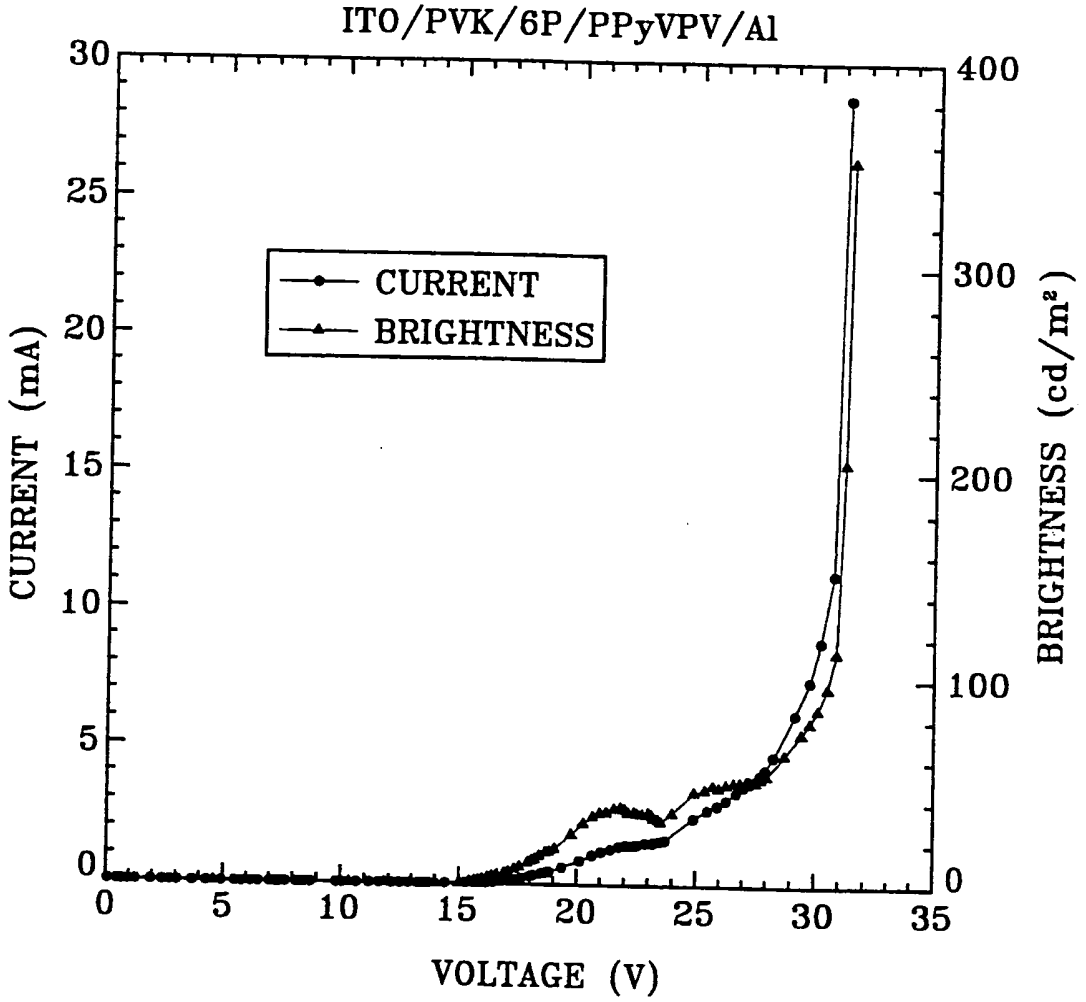


FIG-16

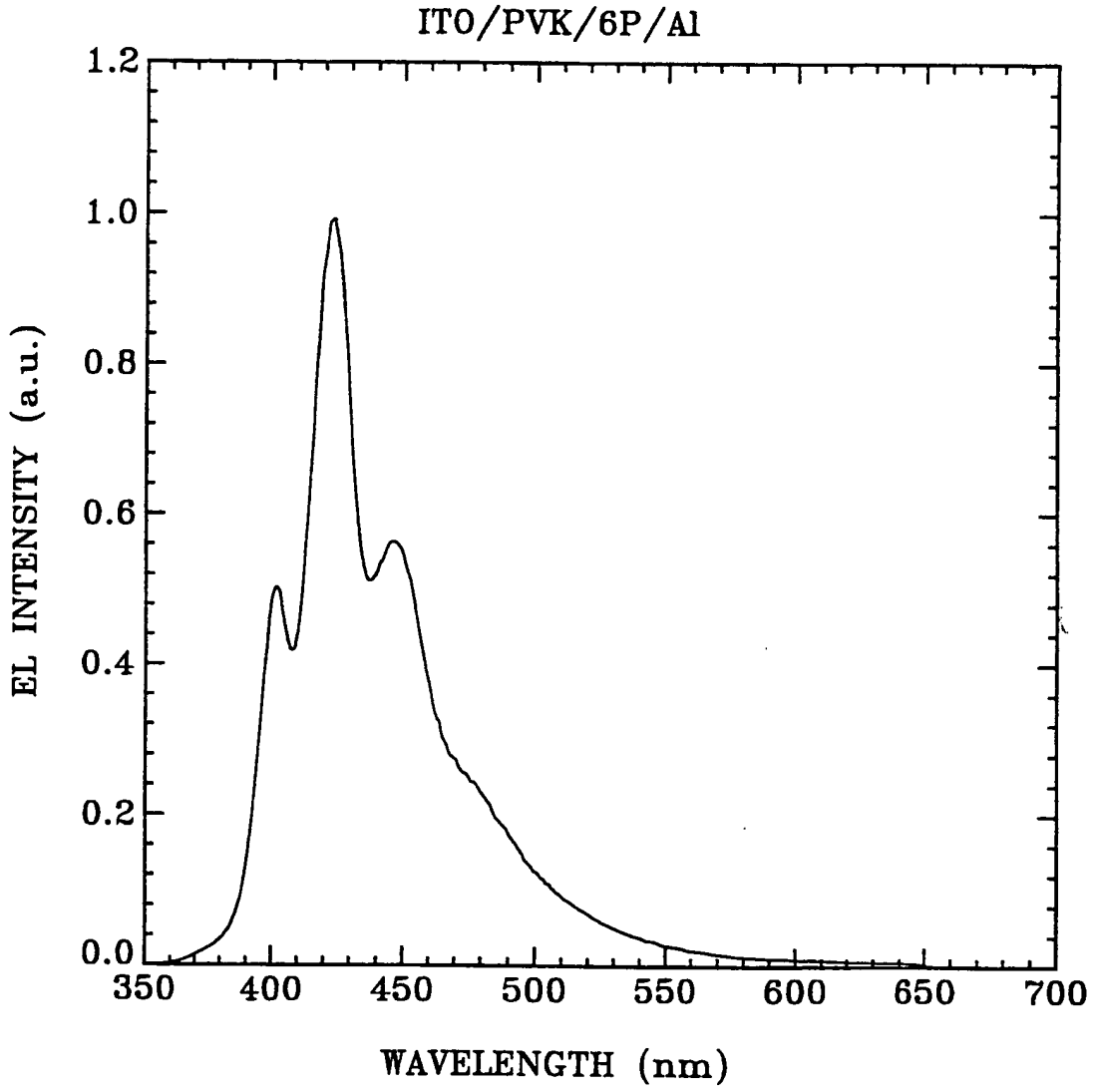


FIG-17

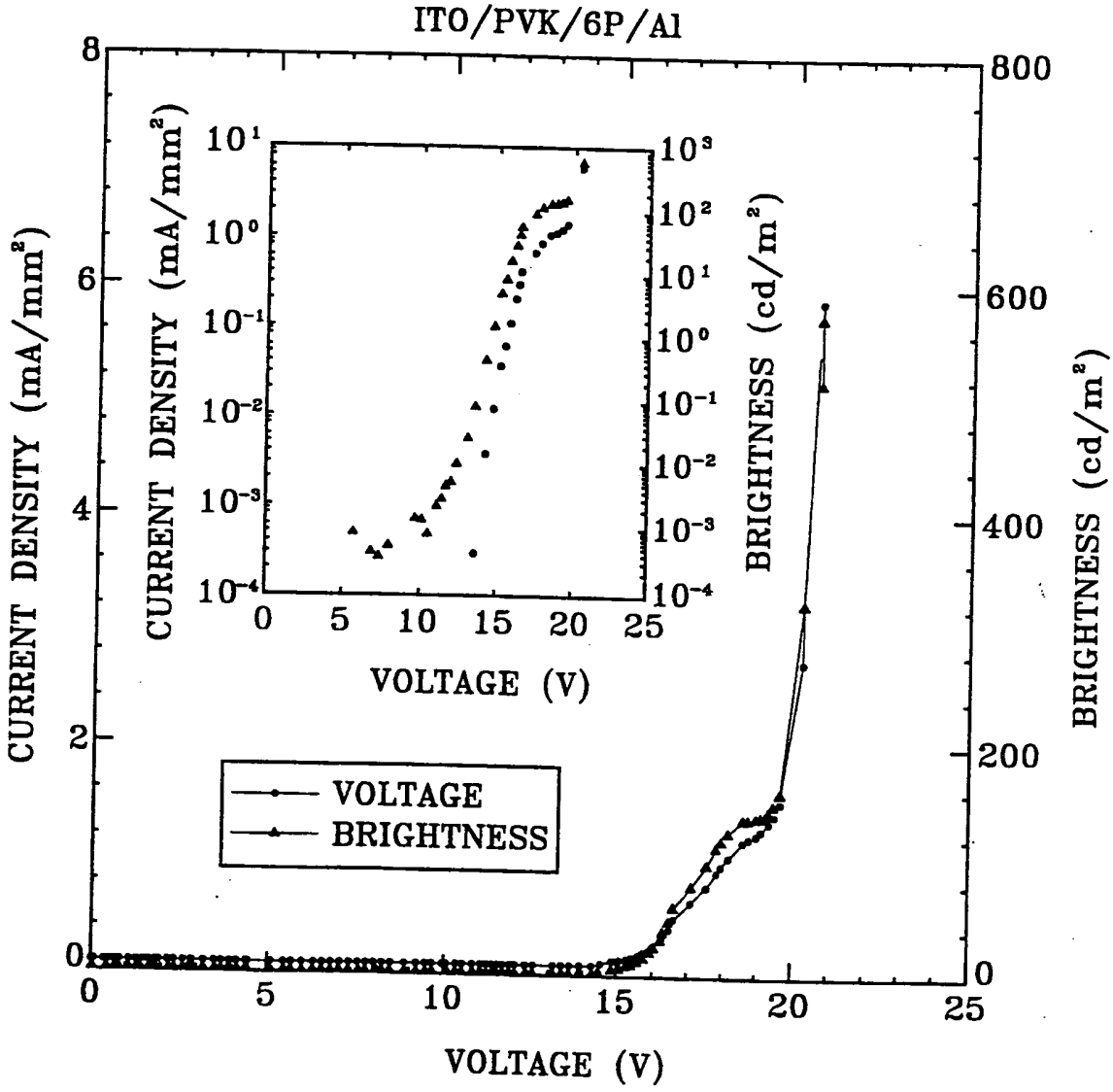


FIG-18

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/06292

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B05D 05/06; H01J 01/62
US CL :313/501, 504, 506; 427/66; 428/690, 691, 917

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 313/501, 504, 506; 427/66; 428/690, 691, 917

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,663,573 A (EPSTEIN et al) 02 September 1997, see entire document.	1-40
Y	US 5,093,210 A (OHTA et al) 03 March 1992, see entire document.	1-40
Y	US 3,854,070 A (VLASENKO et al) 10 December 1974, see entire document.	1-40

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
30 JUNE 1999	19 JUL 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer BLAINE R. COPENHEAVER Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*